SCIENCE FOR CERAMICS PRODUCTION

SYNTHESIS OF NONSTOICHIOMETRIC ALUMINOMAGNESIUM SPINEL WITH A TETRAGONAL LATTICE (REVIEW)

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The results of x-ray diffraction and IR-spectroscopic studies of samples of nonstoichiometric aluminomagnesium spinel $Mg_{1-x}Al_{2-y}O_{4-z}(OH)_z$ formed after treating aluminomagnesium spinel synthesized by the sol-gel method at temperatures of 800 and 1100°C with concentrated acids, are reported. It was found that three phases of nonstoichiometric aluminomagnesium spinel $Mg_{1-x}Al_{2-y}O_{4-z}(OH)_z$ with tetragonal lattices and a different type of superstructure are formed. The x-ray patterns of the two phases correspond to body-centered lattices with parameters $a = 5.712(3)$ Å, $c = 8.092(3)$ Å, and $a = 5.714(3)$ Å. The x-ray pattern of the third phase was indexed in a primitive tetragonal lattice: $a = 5.718(3)$ Å, $c = 24.261(27)$ Å.

The noble spinel $MgAl_2O_4$ — a mineral of high pressures and temperatures [1] — is encountered in the form of single, developed, octahedral crystals in metamorphic, high-magnesium rocks, has high hardness (7.5 – 8.0 on the Moos scale), and despite the low atomic mass of magnesium and aluminum, high density (3.59 g/cm^3). Due to the possibility of substituting Mg^{2+} and Al^{3+} with transition metal ions ($Mg^{2+} \rightarrow Fe^{2+}$, Fe^{3+}, Mn^{2+}, Co^{2+}; $Al^{3+} \rightarrow Fe^{3+}$, Cr^{3+}, V^{3+}, Mn^{3+}, Fe^{2+}), many varieties are found in nature [2]. The best known are ceylonite — a spinel of intermediate composition between $MgAl_2O_4$, and hercynite $FeAl_2O_4$; chlorspinel — a bright green variety of intermediate composition between noble spinel and magnesioferrite $MgFe_2O_4$ containing up to 7.2 wt.% Fe_2O_3; chromspinel (composition intermediate between spinel and picrochromite $MgCrO_4$); gahnospinel — with a composition intermediate between spinel and gahnite $ZnAl_2O_4$. Aluminomagnesium spinels enriched with vanadium, nickel, cobalt, and manganese have been found. With respect to the variety of tints and shades of color, noble spinel is as good as multicolored corundum. Ruby spinel — bright red, pink, and pinkish-red, purple-red, and orange-red — is especially distinct among jewelry spinels. An alexandrite-like spinel whose color varies from violet in daylight to reddish-violet in artificial light, and "star spinel," whose asterism is due to microscopic rutile needle inclusions have been described.

Pigments based on solid solutions of (Mg, Fe) [Al, Ti, Cr, Fe]$_2$O$_4$ are widely used for decorating ceramic ware.

The structure of noble spinel is of the type of structures incorporated in very close packing of atoms of the same size. The first studies of the structure of $MgAl_2O_4$ (1915) showed that it is a derivative of cubic three-layer very close packing with filled tetrahedral and octahedral vacancies. There are eight formula units ($Z = 8$) — $Mg_8Al_{16}O_{32}$ — per unit cell.

The structure of noble spinel is described by Fedorov symmetry group Fd3m. Structurally equivalent positions 8(a) A, 8(b) A*, 48(f) A** correspond to 64 tetrahedral vacancies in it; 16(d) B, 16(c) B* correspond to 32 octahedral vacancies. Magnesium ions occupy octuple position 8(a) with point symmetry 43m; aluminum ions occupy centrosymmetric positions 16(d) and are on third-order axes (3m); oxygen ions forming close cubic packing occupy monovariant positions 32(e) and are also found on third-order axes (3m). In selecting the origin at point 3m, the ions constituting the structure of the spinel have the following coordinates:

$$Mg^{2+} - 8(a) - 1/8 \; 1/8 \; 1/8;$$

$$Al^{3+} - 16(d) - 1/2 \; 1/2 \; 1/2;$$

$$O^{2-} - 32(e) - x \; x \; x$$

for $x \approx 0.2598$.

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TABLE 1

MgO : Al_2O_3 ratio	Lattice parameter, Å	Refractive index
1 : 1	8.078	1.7189
1 : 2	7.985	1.7251
1 : 3	–	1.7264
1 : 3.5	7.964	–
1 : 4	–	1.7284
1 : 5	–	1.7288

The structure of $MgAl_2O_4$ has octahedral layers (111) perpendicular to the third-order axes, in which the octahedral vacancies are 3/4 filled with aluminum ions according to the spinel law. These layers alternate with antispinel octahedral layers 1/4 filled with vacancies [3, 4].

When tetrahedral vacancies (A position) are filled with Mg^{2+} ions and octahedral (B position) are filled with Al^{3+} ions, the same migration of four oxygen ions takes place. As a result of this, the volume of tetrahedral vacancies increases and the volume of octahedral vacancies decreases.

Oxygen parameter U, which determines the position of the O^{2-} ion in the lattice, is used as the quantitative characteristic of oxygen ion migration. For an ideal cubic face-centered lattice, oxygen parameter U is equal to 0.375. According to neutron diffraction data, $U = 0.3873$ m [5]. The oxygen parameter, vacancy size (R_A, R_B) and unit cell parameter a of $MgAl_2O_4$ are correlated by the following relations:

$$R_A = (U - 0.250)a\sqrt{3 - r_o};$$

$$R_B = (0.625 - U)a - r_o,$$

where r_o is the radius of the oxygen ion, equal to 1.36 Å.

In the structure of the spinel, each oxygen ion is bound with one Mg^{2+} cation and three Al^{3+} cations. In the immediate vicinity of the Mg^{2+} ion, there are four oxygen ions at a distance of 1.91 Å and four octahedral vacancies at a distance of 1.77 Å in directions $[\bar{1}\,\bar{1}\,\bar{1}]$, $[\bar{1}\,\bar{1}\,1]$, and $[\bar{1}\,1\,1]$. Direction $[\bar{1}\,\bar{1}\,\bar{1}]$ is the most favorable for diffusion of Mg atoms when the temperature rises. The Al^{3+} ion is surrounded by six O^{2-} ions at a distance of 1.97 Å and two tetrahedral vacancies at a distance of 1.77 Å in directions [111] and $[\bar{1}\,\bar{1}\,\bar{1}]$. Crimped "channels" consisting of alternating octahedral vacancies and tetrahedral vacancies filled with Mg^{2+} can be distinguished in the structure of the spinel. Each cation in the octahedral position is surrounded by four such channels [3, 4].

The studies of the structure of spinels showed that cations can be distributed over positions A and B in several variants. If A^{2+} cations occupy position 8(a) and B^{3+} cations occupy position 16(d), this cation distribution is called normal $A[B_2]O_4$. Chromite $(Mg, Fe)[Cr_2]O_4$ and francolite $Zn[Fe_2]O_4$ are normal spinels. If the B^{3+} cation occupies tetrahedral position 8(a), while cations A^{2+} and B^{3+} are randomly distributed in octahedral vacancies, this distribution is called inverse and the spinel is inverse (inverted) $B[AB]O_4$. Ferrites $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$ are inverse spinels.

Many spinels are characterized by intermediate degrees of inversion i: $B_iA_{1-i}[B_{2-i}A]O_4$. The degree of inversion is a function of both the composition and the temperature. Magnesioferrite $MgFe_2O_4$ can vary i within wide limits and at high temperatures, the distribution becomes random: $i = 0.67$.

Al^{27} NMR [5] and EPR [6] studies of natural samples of noble spinel with incorporation of Cr^{3+} impurity showed that the cation distribution over positions A and B corresponds to an almost normal spinel ($i \sim 0.04$) $Mg_{0.96}Al_{0.04}[Mg_{0.04}Al_{1.96}]O_4$. Cell parameter $a = 8.089$ A [4]. A spinel grown from melts becomes partially inverse. This is because a phase transition of the second kind takes place in the $600 - 700°C$ temperature range [7, 8]. As a result of cation exchange, the structure of the spinel becomes partially inverse: $Mg[Al_2]O_4 \rightarrow Mg_{1-i}Al_i[Mg_iAl_{2-i}]O_4$. Heating the spinel above 800°C causes a significant increase in the inversion parameter at 1600°C, and the inversion parameter reaches 0.157. Unit cell parameter a decreases with an increase in the degree of inversion i. This parameter is equal to 8.0806 Å for a noble spinel synthesized from a melt at 900°C, and it decreases to 8.0788 Å after annealing for 4 days at 1200°C [8].

In the $MgAl_2O_4 - Al_2O_3$ system, solid solutions with a spinel structure up to a MgO : Al_2O_3 ratio equal to 1 : 5 were found for the first time in [9]. With an increase in the aluminum content, the unit cell parameter of aluminomagnesium spinel decreases [10 – 14], but the refractive index [9] increases. The values of a for crystals of aluminomagnesium spinel of different composition grown by the Verneuille method are reported in Table 1 [10, 11]. The refractive index values are taken from [9].

The crystal-chemical data for the ideal composition of $MgAl_2O_4$ and with an excess of aluminum oxide are shown in Table 2 [12]. A higher unit cell parameter — $a = 8.0878$ Å — is reported in [15] for crystals of nonstoichiometric aluminomagnesium spinel of $MgO \cdot 3Al_2O_3$ composition grown by the Chochralski method.

At high temperatures, formation of solid solutions of aluminum oxide in spinel is observed in the $MgO \cdot Al_2O_3$ system [10]. The structures of the nonstoichiometric spinels that exist at high temperatures are described by the general formula $Mg_{1-3x}[Al_{2+2x}]\square_xO_4$ [14].

At temperatures above 1200°C, nonstoichiometric aluminomagnesium spinel δ-$MgAl_{26}O_{40}$ with a tetragonal lattice and parameters close to the parameters of δ-Al_2O_3 was found in [14, 16]: $a = 7.956$ (Å), $c = 11.745$ (Å). The limiting composition of this phase corresponds to dissolution of approximately 40% (molar content) δ-Al_2O_3 in the spinel. The crystal chemical formula of this spinel is $Mg_5Al_{18}\square O_{32}$ [14]. Three of the eight tetrahedral positions are thus vacant, but then two additional octahedral nonspinel B^* occupied positions and one vacancy appear.

The structure of $MgAl_2O_4$ is very similar to the cation-defective spinel γ-$Al_{8/3}O_4 - Al_{0.67}\square_{0.33}[Al]_2O_4$. γ-$Al_{8/3}O_4$ synthesized from crystallized boehmite at $450 - 500°C$ con-

tains up to 2 wt.% structurally bound water. This is manifested in the x-ray patterns of γ-$Al_{8/3}O_4$ by slight tetragonal distortion of the cubic face-centered lattice: the most intensive lines with indexes hkl equal to 400 and 440 are split into two 400 and 004 and 440, 044, which corresponds to a F-face-centered tetragonal lattice with $a = 7.95$ Å and $c = 7.79$ Å [17, 18]. The degree of tetragonal distortion of the lattice (a/c) of the γ-oxide becomes greater with an increase in the water content [18, 19].

In refining the structure of low-temperature aluminum oxides, Al^{3+} ions were found in positions 8(b) A^* and 16(c) B^* in [20], which cannot be filled in the structure of an ideal spinel. According to the data in [19], γ-$Al_{8/3}O_4$ has the structural formula:

$$A^*_{1.75}A_{6.72}[B^*_{1.0}B_{9.0}]O_{23.5}(OH)_{8.5}.$$
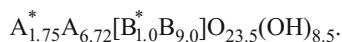
Low-temperature metastable aluminum oxides like γ-$Al_{8/3}O_4$ are protospinels — compounds intermediate between oxides and hydroxides — with the general formula:

$$A^*_{x1}A_{x2}[B^*_{y1}B_{y2}]O_{32-z}(OH)_z.$$
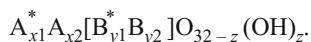
After annealing for 8 weeks at 800°C, γ-$Al_{8/3}O_4$ is converted to a new phase — δ-Al_2O_3 [19].

In contrast to γ-oxide, ordering of vacancies by octahedral positions is observed in δ-Al_2O_3: $Al[Al_{1.67}\square_{0.33}]O_4$. This is manifested in the x-ray pattern by a large number of superstructural lines. On the whole, the x-ray pattern of δ-Al_2O_3 corresponds to a tetragonal lattice in which subcell parameter c_0 (7.81) is tripled: $a = 7.954$ Å, $c = 3c_0 = 232.34$ Å, $c/3a = 0.981$. The lattice parameters of δ-Al_2O_3 were subsequently refined in [21]: $a = 5.599$ Å, $c = 23.657$, Fedorov group $P\bar{4}m2$.

In coprecipitation of aluminum hydroxide and magnesium nitrate followed by calcination at 100°C, the aluminomagnesium spinel of nonstoichiometric composition $Mg_{0.36}Al_{2.44}O_4$ (9% MgO, 91% Al_2O_3, mass content) with unit cell parameter $a = 8.975$ A, was synthesized. The cation distribution in the structure of the aluminomagnesium spinel was refined by full-profile analysis: $(Mg_{0.36}Al_{0.6})A^*_{0.05}[Al_{1.72}B^*_{0.05}]O_4$ [22].

In comparison to a spinel of stoichiometric composition, there is approximately 1/3 Mg^{2+} and 2/3 Al^{3+} ions in tetrahedral position 8(a); the octahedral positions are approximately 85% occupied; some of the cations are in positions A^* and B^*, uncharacteristic of spinel, as in the structure of γ-$Al_{8/3}O_4$.

An x-ray diffraction study of formation of low-temperature solid solutions and nonstoichiometric spinels in the $MgO - Al_2O_3$ system was conducted in [13]. The results of the study were examined based on the protospinel structure $Al^*_{1.75}Al_{6.75}[Al^*_{1.0}Al_{9.0}]O_{23.5}(OH)_{8.5}$. Several variants of the position of Mg^{2+} cations in the structure of γ-$Al_{8/3}O_4$ were examined. As a result, it was concluded that inclusion of magnesium cations in the structure of solid solutions does

TABLE 2

Atomic content, %		Unit cell parameter, Å
Mg	Al	
0.100	2.000	8.084
0.900	2.067	8.068
0.800	2.133	8.049
0.700	2.200	8.031
0.600	2.266	8.012
0.500	2.333	7.996
0.450	2.367	7.982
0.400	2.400	7.975
0.350	2.433	7.969

not occur due to random substitution of Al^{3+} by Mg^{2+}. The amount of filled tetrahedral positions of spinel type 8(a) increases in the first stage. As a result, the number of occupied "nonspinel" octahedral positions decreases, and partial substitution of Al^{3+} cations by Mg^{2+} is subsequently observed.

In incorporation of up to 7 wt.% MgO in the structure, a solid solution described by the following formula is formed:

$$Al^*_{1.75}Al_{6.75}Mg^*_{0.5}Mg_{1.25}[Al_{9.0}]O_{22.5}(OH)_{9.5}.$$
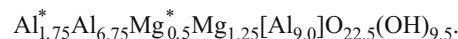
All 8(a) positions A are thus totally occupied, and of the 16(d) octahedral positions B, only 9 are occupied. Of the "nonspinel", tetrahedral positions A^* are 1.75 occupied by aluminum. Gradual substitution of aluminum by magnesium in A positions then takes place. This causes an increase in the number of hydroxyl groups OH^-. In addition, Al^{3+} ions migrate from positions A^* and A to octahedral positions B, which significantly reduces the number of OH^- groups. In incorporation of more than 7 wt.% MgO, the structural formula describing the solid solution at 100°C will be:

$$Al^*_{1.75-y}(Mg, Al)_8Al_{9.0+4y}O_{22.5+x}(OH)_{9.5-x}.$$
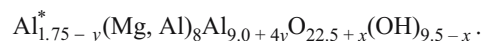
When the magnesium content increases in the solid solution, its structure approaches the spinel structure: the number of Al^{3+} ions in positions B increases, so that the number of OH^- groups decreases. At a 28 wt.% MgO content, all spinel tetrahedral positions will be occupied by Mg^{2+}, and Al^{3+} cations will go from positions A^* and A to positions B, and at 1200°C, the stoichiometric spin $MgAl_2O_4$ is formed.

According to the data in [13], the following phase transitions take place in synthesis of the noble spinel $MgAl_2O_4$ in the 550 – 1200°C temperature range:

$$Al^*_{1.75}Al_{6.75}[Al^*_{1.0}Al_{9.0}]O_{23.5}(OH)_{8.5} \xrightarrow[+Mg^{2+}]{550\,°C}$$

$$Al^*_{1.75}Al_{6.75}Mg^*_{0.5}Mg_{1.25}[Al_{9.0}]O_{22.5}(OH)_{9.5} \xrightarrow[+Mg^{2+}]{1000\,°C}$$

$$Al^*_{1.75-y}(Mg, Al)_8Al_{9.0+4y}O_{22.5+x}(OH)_{9.5-x} \xrightarrow[+Mg^{2+}]{1200\,°C} MgAl_2O_4.$$
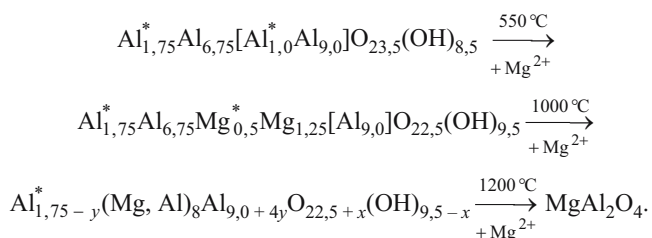
TABLE 3

Composition of batch, %[*]	Phase composition after annealing at		Lattice parameter, Å	Refractive index
	800°C	1100°C		
40% Al_2O_3	$MgAl_2O_4$ MgO (little)	–	8.084	1.716
60% MgO	–	$MgAl_2O_4$ MgO (little)	8.084	1.718

[*] Molar content.

TABLE 4

Synthesis temperature, °C	Phase composition after treatment with acids and annealing at 600°C	Lattice parameter, Å	
		a	c
800	$Mg_{1-x}Al_{2-y}O_{4-z}(OH)_z$	5.712[*]	8.092[*]
		5.723	8.086
		5.714	18.833
	$Mg_{1-x}Al_{2-y}O_{4-z}(OH)_z$ α-Al_2O_3 (much)	5.724	24.261
1100	$Mg_{1-x}Al_{2-y}O_{4-z}(OH)_z$ α-Al_2O_3 (little)	5.725	8.089

[*] Treatment for 24 h.

Synthesis of aluminomagnesium spinel with an excess of 10% (molar content) magnesium oxide at 800 and 1100°C with and without TiO_2 and Na_2O additives was described previously in [23]. The results of x-ray diffraction and IR spectroscopic studies of the samples of aluminomagnesium spinel with no additives synthesized in [23] are reported

here. The free MgO in the samples was removed with acids at room temperature.

The samples of $MgAl_2O_4$ treated with acids for two days were washed on a filter with distilled water, dried at 100°C, and calcined at 600°C for 1 h.

The x-ray phase analysis of the samples was conducted in monochromatized $CuK\alpha_1$ radiation in a Huber Imaging Plate Guiner Camera and a FR-552 camera (germanium internal standard).

The petrographic analysis was conducted in transmitted light in a Polam R-211 polarizing microscope.

The IR spectra were made on a Perkin-Elmer 983-G (Sweden). Powders treated with acids were placed between two dry fluorite windows and held in a holder. The IR spectra were made in the fluorite transparency region, 4000 – 1200 cm^{-1}.

The results of the x-ray phase analysis are reported in Tables 3 – 5. Only lines of the spinel phase are present in the x-ray patterns of samples synthesized at 800°C and treated with concentrated HF, HCl, HNO_3, and H_2SO_4. A small number of α-Al_2O_3 lines of low intensity was found in the x-ray pattern of the sample made at 100°C and treated with concentrated HCl. The diffractograms of the sample synthesized at 800°C and treated with concentrated HCl for 2 days exhibited a much larger number of α-Al_2O_3 lines (see Table 4).

The presence of corundum in the samples treated with the concentrated acids indicates perturbation of the stoichiometry of the synthesized aluminomagnesium spinel.

The x-ray patterns of the samples treated with the acids could not be indexed in a cubic face-centered lattice. The x-ray patterns of the samples of $MgAl_2O_4$ fabricated at 800°C and treated with concentrated HF, HCl, and H_2SO_4

TABLE 5

I			II			III		
I	d_e, Å	hkl	I	d_e, Å	hkl	I	d_e, Å	hkl
28	4.6900	1 0 1	36	4.6688	1 0 3	10	4.6982	0 0 4
31	2.8666	2 0 0 1 1 2	29	2.8644	2 0 0 1 1 6	10	2.8612	0 2 0
100	2.4436	2 1 1	100	2.4435	0 1 9 1 2 3	100	2.4419	2 0 4
3	2.3348	2 0 2	–	–	–	–	–	–
66	2.0244	2 2 0	79	2.0227	2 2 0	50	2.0209	2 2 0
8	1.6520	3 1 2	8	1.6499	3 1 6 2 0 12	–	–	–
38	1.5572	3 0 3	37	1.5561	2 3 3 3 0 9	40	1.5547	3 0 7 2 3 3
78	1.4301	2 2 4	90	1.4295	2 2 12 0 4 0	60	1.4282	0 4 0
3	1.3685	4 1 1	–	–	–	–	–	–
2	1.2785	1 1 6	3	1.2783	1 1 18 3 3 6	–	–	–
1	1.2334	3 0 5	–	–	–	–	–	–
1	1.2202	4 2 2	–	–	–	–	–	–
–	–	–	9	1.1672	0 4 12	–	–	–

were indexed in a tetragonal body-centered I lattice. The lattice parameters of the samples treated with HF and H_2SO_4 were equal to: $a = 5.723(3)$ Å, $c = 8.086(3)$ Å, and for treatment with HCl for 24 h, $a = 5.712(3)$ Å, $c = 8.092(3)$ Å (see Table 5, I). The lattice with $a = 5.723$ Å, $c = 8.086$ Å is a derivative of pseudocubic (tetragonal) face-centered F with $a = 8.084$ Å, $b = 8.084$ Å, $c = 8.094$ Å. Going from the I-tetragonal cell to F is described by the matrix:

$$\begin{vmatrix} 0 & 0 & -1 \\ 1 & -1 & 0 \\ -1 & -1 & 0 \end{vmatrix}.$$

The tetragonal I lattice parameters of the synthesized phases did not differ greatly from the tetragonal lattice parameters of aluminum oxide $Al_{10.666}O_{16}$ ($Al_{8/3}O_4$): $a = 5.6(2)$ Å, $c = 7.854(6)$ Å, Fedorov group $I4_1/amd$, $Z = 1$ (PDF ICDS 80-0956).

The x-ray pattern of the sample of $MgAl_2O_4$ treated with nitric acid corresponded to a body-centered tetragonal lattice with a different parameter c: $a = 5.714(3)$ Å, $c = 18.833(35)$ Å (see Table 5, III). Lattice parameter c can be considered as subcell parameter $c_0 = 4.708$ A increased by 4 times.

The x-ray pattern of the sample of $MgAl_2O_4$ treated with concentrated hydrochloric acid for 2 days is indexed in a tetragonal primitive lattice with parameters $a = 5.718(3)$ Å, $c = 24.261(27)$ Å (see Table 5, II), which insignificantly differ from the parameters of aluminum oxide δ-Al_2O_3 [21]. In this case, too, we can distinguish a subcell with parameters a and $c = 3c_0$ ($c_0 = 8.087$ Å). The lack of multiplicity between the values of subcell parameter c_0 of the phases formed as a result of treatment with nitric and hydrochloric acids suggests that the structure of the phase formed in treatment with nitric acid cannot be brought to the structure of a spinel with ordered vacancies.

Broad bands at 3500 and 1650 cm^{-1} were identified in the IR spectra of the samples treated with the acids, as for δ-Al_2O_3 [21]. An additional band in the form of a shoulder at 1578 cm^{-1} was found for the sample treated with nitric acid. The first two bands indicate the presence of molecular water and perhaps the presence of a small number of OH$^-$ groups bound with Al^{3+} cations.

The results of the physicochemical study suggest that three phases of nonstoichiometric aluminomagnesium spinel $Mg_{1-x}Al_{2-y}O_{4-z}(OH)_z$ with a tetragonal lattice were formed after treatment of samples of aluminomagnesium spinel synthesized by the sol-gel method at 800 and 1100°C. Two of them are characterized by body-centered tetragonal lattices with different parameters c. The parameters of the primitive tetragonal lattice of the third phase are close to the parameters of δ-Al_2O_3. The structures of these phases are probably homologously related to the structure of γ-$Al_{8/3}O_4$.

We were thus able to synthesize three phases of nonstoichiometric aluminomagnesium spinel with tetragonal lattices and a different type of superstructure for the first time.

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